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REACTIONS OF TRIBUTYLSTANNYL ANIONIODS WITH ALKYL BROMIDES.(U)
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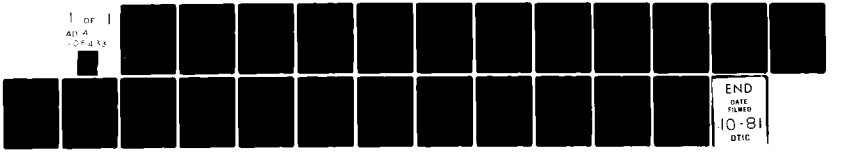

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The reactions of tributylstannyl anionoids (Bu_3SnM, M = Li, K, Cs) with alkyl bromides have been studied. Tributylstannylpotassium and -cesium were prepared by deprotonation of tributyltin hydride with the mixed deprotonating agents potassium (cesium) diisopropylamide/lithium tert-butoxide. The predominant mechanism for alkylation of tributylstannyl anionoids by primary bromides is an S_N2 displacement or its mechanistic equivalent, but the reactions of tributylstannyllithium with two secondary bromides appear to

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involve free radicals as intermediates. Dicyclohexylphosphine, which serves as a trapping agent for intermediate free radicals, was found to react relatively slowly with tributylstannyllithium to give hexabutylditin.

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Reactions of Tributylstannyl Anionoids with Alkyl Bromides

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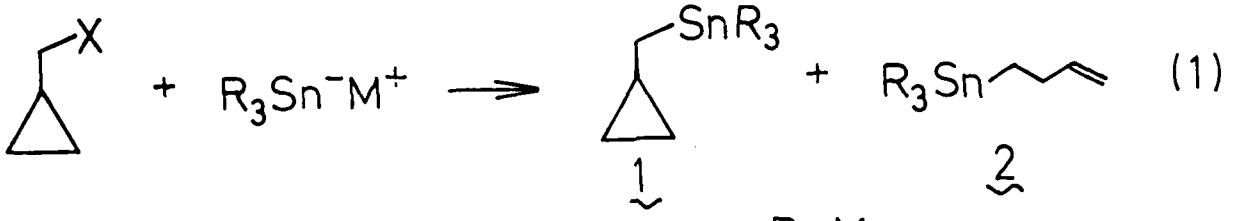
Summary: The reactions of tributylstannyl anionoids (Bu_3SnM, M = Li, K, Cs) with alkyl bromides have been studied. Tributylstannylpotassium and -cesium were prepared by deprotonation of tributyltin hydride with the mixed deprotonating agents potassium (cesium) diisopropylamide/lithium tert-butoxide. The predominant mechanism for alkylation of tributylstannyl anionoids by primary bromides is an S_N2 displacement or its mechanistic equivalent, but the reactions of tributylstannyllithium with two secondary bromides appear to involve free radicals as intermediates. Dicyclohexylphosphine, which serves as a trapping agent for intermediate free radicals, was found to react relatively slowly with tributylstannyllithium to give hexabutylditin.

An interest in the synthesis of unsymmetrical tetraalkyltin compounds has led us to investigate the nature of the reactions of tributylstannyl anionoids with alkyl bromides. Previous mechanistic studies generally employed the archetypal trimethyl- and triphenylstannyl anionoids. Two recent studies probing the mechanisms of trimethylstannyl anionoid reactions with primary bromides resulted in different conclusions. San Filippo, Silbermann, and Fagan found that cyclopropylcarbinyl bromide (iodide) reacted with trimethylstannyl anionoids to give both cyclopropylcarbinyl (1a) and butenyl (2a) products (eq 1).[1] These results imply that a portion of the reactions proceeded by



(1)

1 2

a: R = Me
b: R = n-Bu

electron transfer from the tin anioniod to the cyclopropylcarbinyl halide to give ultimately free cyclopropylcarbinyl radical which rearranged to the 1-buten-4-yl radical. Kuivila has used dicyclohexylphosphine as a free radical trapping agent in studies of the reactions of trimethylstannylsodium with alkyl bromides.[2] These results suggest that no free radicals were formed in the reaction of n-butyl or isobutyl bromide with trimethylstannylsodium, although a portion of the reaction with neopentyl bromide may involve electron transfer to the halide. We report the application of these two methods to the study of reactions of tributylstannyl anionoids with primary bromides. Neither method gave unequivocal results, but, consistent with the findings of others,[2,3] both indicate that the predominant pathway for these reactions involves an S_N2 displacement or its mechanistic equivalent in which intermediate free anions or radicals are not formed.

Results and Discussion

Samples of tributylstannyllithium in tetrahydrofuran (THF) were prepared by conventional metalation of tributyltin chloride and by deprotonation of tributyltin hydride with lithium diisopropylamide (LDA).[4] Tributylstannylpotassium was prepared by the method of Corriu[5] by deprotonation of tributyltin hydride with potassium hydride and by deprotonation of tributyltin hydride with the mixed reagent potassium diisopropylamide/lithium tert-butoxide.[6] Tributylstannylcesium was prepared by deprotonation of tributyltin hydride by the mixed reagent cesium diisopropylamide/lithium tert-butoxide; we are not aware of a previous report of this mixed deprotonating agent.

The use of mixed deprotonation agents deserves comment. In our hands deprotonation of tributyltin hydride with potassium hydride[5] was not successful when we used potassium hydride from one supplier. We obtained mainly hexabutylditin, presumably from the reaction of tributylstannylpotassium with unreacted hydride (vide infra). When potassium hydride from another supplier was used, the preparation of tributylstannylpotassium was successful. It is possible that in the latter case the initial product formed was hexabutylditin which subsequently reacted with potassium hydride to give the desired reagent since Corriu observed that hexaphenylditin reacts with potassium hydride to give triphenylstannylpotassium.[5] Regardless of the course of the potassium hydride reaction, treatment of tributyltin hydride with the reagent potassium diisopropylamide/lithium tert-butoxide produced the desired tributylstannyl anionoid readily at low temperatures. From the alkylation results we obtained there appears to be little difference between the stannylpotassium reagents prepared by these two procedures. We conclude that the stannylpotassium and cesium reagents are more easily prepared from the mixed deprotonation reagents.

Kuivila et al. have presented a strong case for the utility of tert-butylamine (TBA) and dicyclohexylphosphine (DCP) as trapping agents for

intermediates in reactions of organic halides with trimethylstannylsodium.[2] In one of their control experiments, they found that DCP does not react with trimethylstannylsodium. We have found that tributylstannyllithium does react relatively slowly with DCP in THF. Thus, in a ^{13}C NMR study, we observed that 0.7 N tributylstannyllithium in THF at -20 ^{o}C reacted with a twofold excess of DCP with a halflife greater that 10 minutes. The major product observed by ^{13}C NMR spectroscopy was hexabutylditin. This result is somewhat surprising when one considers the reported pKa's of tributyltin hydride (pKa = 25.0 in dimethoxyethane)[7] and dicyclohexylphosphine (pKa = 36 in THF),[8] and the reaction may not occur via an initial proton transfer. Nevertheless, the reaction of DCP with tributylstannyllithium is too slow to have a profound effect on the results of alkylation reactions with primary alkyl bromides. In similar ^{13}C NMR studies at -20 ^{o}C, the reactions of 0.7 N tributylstannyllithium with n-butyl bromide and with cyclopropylcarbinyl bromide were complete in less than 0.5 minutes. As a further test of the relative rates of reactions of tributylstannyllithium with DCP and a primary alkyl bromide, we compared the product yields obtained from the reaction of tributylstannyllithium with n-octyl bromide in the absence and presence of DCP. The results are collected in Table 1. When no DCP was present, we obtained the alkylation product in

(INSERT TABLE 1)

in high yield. Addition of 1.0 and 4.0 equivalents of DCP to the n-octyl bromide (Runs 2 and 3) gave somewhat lower yields of alkylation product. When 1.0 and 4.0 equivalents of DCP were added to the tributylstannyllithium reagent and the resulting mixtures were allowed to stand at -20 ^{o}C for 5 minutes before addition to the bromide (Runs 4 and 5), the yields of alkylation product were not substantially altered. Thus, DCP has a minor effect on the yields in this

alkylation reaction, but this is not due to consumption of a large amount of the stannyllithium reagent.

Cyclohexyl bromide also reacted faster with tributylstannyllithium than did DCP. Thus, the reaction of 0.5 N tributylstannyllithium with a two-fold excess of cyclohexyl bromide at -20 ^{o}C was found to be essentially complete within 5 minutes (Table 2, Runs 1-5). The fact that tributylstannyllithium

(INSERT TABLE 2)

reacts relatively rapidly with cyclohexyl bromide permitted us to study the effect of DCP on the reaction of this secondary bromide by the method of Kuivila.[2] The results, given in Table 2, Runs 6-12, are similar to those observed in the reaction of trimethlystannylsodium with cyclohexyl bromide.[2] Specifically, the addition of tert-butylamine had virtually no effect on the yield of tributyl(cyclohexyl)tin. This is expected since our solutions of tributylstannyllithium already contained diisopropylamine. However, addition of DCP dramatically lowered the yield of alkylation product. Similarly, the alkylation of tributylstannyllithium by cylcobutyl bromide was strongly inhibited by the addition of DCP. Specifically, with zero, two, and four equivalents of DCP added to the halide, the yield of tributyl(cyclobutyl)tin decreased from 69 to 22 to 10%, respectively, as the yields of hexabutylditin increased (13, 63, 81%, respectively). These results are consistent with a major portion of the reactions of these secondary bromides proceeding through free radicals which are trapped by DCP.

Cyclopropylcarbinyl bromide was allowed to react with tributylstannyl anionoids both in the absence and presence of the trapping agents TBA and DCP. The use of this bromide as a probe is complicated by the fact that both 4-bromo-1-butene and bromocyclobutane are formed in small amounts in the synthesis of this halide.[9] For our samples of this bromide, we determined the amount of 4-bromo-1-butene by ^{1}H NMR spectroscopy and the amounts of both contaminants by gc. In various preparations we observed a 1-3% impurity of 4-bromo-1-butene and a ca. 6% impurity of bromocyclobutane. For the reactions we studied, the bromocyclobutane impurity was not important since we found that tributylstannyllithium reacts with one equivalent of bromocyclobutane at -20 ^{o}C in THF to give <0.3% yield of ring-opened product 2b. 4-Bromo-1-butene, of course, does give acyclic product 2b in high yield in reactions with tributylstannyl anionoids. Thus, we believe it is advantageous not to use a large excess of halide in these types of studies. For the reactions we studied, the yields of ring-opened alkylation product 2b were typically several times greater than the maximum amount which could be formed from alkylation of the tributylstannyl anionoid by the 4-bromo-1-butene impurity.

Reactions of tributylstannyl anionoids with 1.0 molar equivalent of cyclopropylcarbinyl bromide in THF at -20 ^{o}C in the absence or presence of trapping agents gave both the cyclic (1b) and ring-opened (2b) alkylation products in 36-79% yield. The remainder of the tin was present as tetrabutyltin (3-28%) and hexabutylditin (up to 49%). Table 3 contains the results of

(INSERT TABLE 3)

several experiments. To test whether lithium tert-butoxide present in the tributylstannylpotassium and -cesium reagents prepared with the mixed deprotonation reagents had an effect on the alkylations, one set of alkylations with tributylstannyllithium contained added lithium tert-butoxide.

From the results in Table 3, it is clear that TBA had virtually no effect on the reaction of tributylstannyl anioniods with cyclopropylcarbinyl bromide. DCP slightly lowered the yield of alkylation products in these reactions as it did in the alkylation of tributylstannyllithium with n-octyl bromide. DCP appears to have a slightly more pronounced effect on the yield of ring-opened product 2b than on that of 1b, however, the dramatic reduction in yield seen in the case of the tributylstannyllithium alkylation with secondary bromides is not present here. These results show that the major pathway for reactions of tributylstannyl anionoids with cyclopropylcarbinyl bromide involves an S_N2 displacement or an equivalent reaction occurring within a solvent cage. The facts that some ring-opened product 2b was obtained and that the yield of 2b was lowered by a larger percentage than that of 1b by addition of DCP suggest that a minor pathway for the reaction could involve free radicals. However, both methods for studying the mechanisms of trialkylstannyl anionoids have limitations which equivocate conclusions concerning minor reaction pathways. Dicyclohexylphosphine reacts with tributylstannyllithium so small changes in alkylation yields could arise from this reaction, especially when large excesses of DCP are used. For cyclopropylcarbinyl bromide, the inherent lack of purity in the samples limits the utility of this probe. Further, the fact that DCP fails to suppress the yield of acyclic 2b in the reaction of tributylstannyl anionoids with cyclopropylcarbinyl bromide to the same extent that it did in the reactions of the secondary bromides is disturbing since the rate of rearrangement of the cyclopropylcarbinyl radical requires that the species escapes from a solvent cage.[10] One speculative explanation of this result is that a tributylstannyl anionoid may react with cyclopropylcarbinyl bromide to give ring-opened 2b by an unusual associative process such as direct attack at the ring carbon in a homo S_N2' reaction.

Hexabutylditin was formed in the alkylation reactions as well as in the reaction of DCP with tributylstannyllithium. Similar results have been reported in other studies.[3b,c,f] The coupled byproduct would be expected to form from the reaction of tributylstannyl anionoid with any tributylstannyl bromide fromed during an alkylation reaction, but it also can be formed from the reaction of tributylstannyl anionoid with tributyltin hydride or by a radical process as pointed out by Kitching.[3f] We have observed in ^{13}C NMR studies that tributyltin hydride reacts over the period of several hours with potassium tert-butoxide in THF at 25 ^{o}C to give hexabutylditin quantitatively; no tributylstannylpotassium was detected during the course of these reactions.[11] Similarly, although tributylstannyllithium reacts with n-octyl bromide to give the alkylation product in high yield (Table 1), the addition of only 0.5 molar equivalents of LDA to tributyltin hydride followed by addition of this mixture to n-octyl bromide gave the alkylation product in only ca. 50% yield and hexabutylditin as the major product detected (40-50%).[11] Thus it is possible that a major portion of the hexabutylditin formed in our alkylation reactions arises from the reaction of tributylstannyl anionoid with tributyltin hydride produced during the reaction.

The apparently facile reaction of tributyltin hydride with tributylstannyl anionoids which we observed explains why carbon bases (i.e. n-butyllithium) cannot successfully deprotonate tributyltin hydride.[4] We have confirmed this observation and found that the only product formed in the reaction of tributyltin hydride with n-butyllithium followed by addition of the mixture to n-octyl bromide is tetrabutyltin (100% yield).[11] Due to the low kinetic basicity of an alkyllithium relative to its nucleophilicity, n-butyllithium probably deprotonates tributyltin hydride slowly to give some tributylstannyllithium which then reacts with excess hydride to give hexabutylditin. Subsequent reaction of

the hexabutylditin thus formed with n-butyllithium would generate tetrabutyltin and tributylstannyllithium[4] which can reenter the cycle in another reaction with tributyltin hydride. Such a scheme preducts, in accordance with our observation, that large amounts of tetrabutyltin will result from the reaction.

Experimental Section

General. All reactions involving organometallic reagents were run in oven-dried glassware under nitrogen or argon. Transfers were made by syringe. Tetrahydrofuran (THF) was distilled from potassium--benzophenone under nitrogen immediately before use. n-Butyllithium in hexane, dicyclohexylphosphine, potassium tert-butoxide, and most of the alkyl bromides were obtained from Aldrich Chemical Co. (bromocyclobutane was obtained from Ash Stevens) and were used without further purification. Diisopropylamine (Aldrich) and tert-butylamine (Aldrich) were distilled from calcium hydride under nitrogen and were stored over 3A molecular sieves. Tributyltin chloride (Ventron), hexabutylditin (Ventron), lithium wire containing 1% sodium (Ventron), cesium tert-butoxide (Callery), and potassium hydride (Ventron and Fluka) were used as obtained. Tributyltin hydride, prepared by the lithium aluminum hydride reduction of the chloride, was distilled from calcium hydride and was stored under nitrogen at -10 ^{o}C. Cyclopropylcarbinyl bromide was made from the reaction of the carbinol (Aldrich) with phosphorus tribromide.[9] The purity of the cyclopropylcarbinyl bromide samples was determined by ^{1}H NMR spectroscopy and by gc (column A below).

^{1}H NMR spectra were recorded on Varian T-60 and XL-200 spectrometers. ^{1}H-decoupled ^{13}C NMR spectra were recorded on a Varian FT-80 equipped with a variable temperature apparatus. Chemical shifts are reported in δ units relative to Me_4Si, however, for convenience we often measured the ^{13}C NMR chemical shifts relative to the β-carbon of THF which we defined as δ 25.3. Benzene-d_6 was used as an internal lock for the XL-200 and FT-80 spectrometers.

Yields of tetraalkyltin compounds were determined by gc analysis (flame ionization detector) using the following columns: (A) 15 ft by 1/8 in., 3% XF-1150 on 80/100 Chromosorb G at 130-145 °C for reactions of tributylstannyl anionoids with cyclopropylcarbinyl bromide and cyclobutyl bromide, and (B) 8 ft by 1/8 in., 3% SE-30 on 80/100 Chromosorb G for other alkylation reactions. Gc standards were added after the reactions had been worked-up. Yields of hexabutylditin were determined by hplc (254 nm, fixed wavelength detector) on a 250 mm by 4 mm Bio-Sil ODS-10 (Bio-Rad) reverse phase column using a 3:1 mixture of THF/water as the eluent and a flow rate of 1.0 mL/min. In this procedure we calibrated the signal response by using standard solutions of known concentrations of hexabutylditin.

Preparation of Tributylstannyllithium. A. Lithium wire (0.5 g, 0.07 g-atom) was cut into pieces, and these were placed in a 40-mL reaction vessel which was then flushed with argon. The wire cuttings were washed with three 10-mL portions of dry hexane and two 10-mL portions of THF. The vessel was cooled to 0 °C, and to it was added 17 mL of THF and 2.7 mL (10 mmol) of tributyltin chloride. The mixture was stirred at 0 °C for 4-6 h before use.

B. Deprotonation of tributyltin hydride by LDA followed Still's procedure.[4] To 10 mL of THF at -78 °C was added 6.4 mL of 1.6 N n-butyllithium in hexane (10 mmol). Diisopropylamine (1.4 mL, 10 mmol) was added, and the mixture was stirred at -78 °C for 0.5 h. Tributyltin hydride (2.6 mL, 10 mmol) was added to the LDA solution, and the mixture was stirred at -78 °C for 1.5-2.0 h.

Preparation of Tributylstannylpotassium. C. The procedure of Corriu [5,12] was used. Potassium hydride (Fluka, 20% in oil) was washed with four 10-mL portions of dry hexane. Traces of hexane were removed in vacuo, and the weight of KH was determined (0.51 g, 13 mmol). THF (17 mL) and tributyltin hydride (2.7 mL, 10 mmol) were added. The reaction vessel was fitted with a vent needle under nitrogen, and the mixture was stirred at 25 °C for 7-8 h. In a similar procedure with KH supplied by Ventron, we obtained, after an attempted alkylation reaction, no (<10%) tetraalkyltin products and detected hexabutylditin as the major tin-containing product.

D. Method B above was used with the exception that 1.2 g (11 mmol) of potassium tert-butoxide was added to the reaction vessel before the addition of n-butyllithium.

Preparation of Tributylstannylcesium. E. Method B above was used with the exception that 2.4 g (12 mmol) of cesium tert-butoxide was added to the reaction vessel before the addition of n-butyllithium.

Alkylation of Tributylstannyl Anionoids. Dry reaction vessels were purged with argon. The desired alkyl halide (1.0 mmol unless noted) and any desired additive were added to the reaction vessel, and enough THF was added to bring the solution to 2.0 mL. The reaction tubes were cooled to -20 ^{o}C in a constant temperature bath, and 2.0 mL aliquots of the tributylstannyl anionoid solutions (1.0 mequiv) were added slowly. After one h at -20 ^{o}C, the reactions were quenched by the rapid addition of 2 mL of water. Ether was added to the reaction mixtures to bring the volume to 20 mL. Hplc analyses (20 μL) for hexabutylditin were then performed. Octadecane was added for an internal gc standard.

Product Identification. Tributylcyclopropylcarbinyltin (1b) was prepared from the reaction of tributylstannyllithium (Method B) with the mesylate of cyclopropylcarbinol in THF at -20 ^{o}C. A sample of 1b was collected by preparative gc. The ^{1}H NMR and ^{13}C NMR spectra and mass spectrum were consistent with the assigned structure. Authentic 4-(tributylstannyl)-1-butene (2b) was prepared from the reaction of tributylstannyllithium (Method B) with 4-bromo-1-butene. The ^{1}H NMR and ^{13}C NMR spectra, gc retention times, and mass spectra of 2b from the reaction of cyclopropylcarbinyl bromide with tributylstannyllithium matched those of the authetic sample. A sample of tributyl(cyclohexyl)tin prepared from the reaction of cyclohexylmagnesium bromide with tributyltin chloride was identical by ^{1}H NMR, ^{13}C NMR and gc retention times to the sample

from the reaction of cyclohexyl bromide with tributylstannyllithium (Method B). Tributyl(octyl)tin was characterized by its ^{1}H NMR spectrum and gc retention time. Tributyl(cyclobutyl)tin was characterized by its ^{1}H and ^{13}C NMR spectra and gc retention time.

^{13}C NMR studies. All spectra were measured at -20 ^{o}C. Tributylstannyllithium (Method A) solutions (2.0 mL, 1.0 N) in THF were transferred to argon purged NMR tubes fitted with septa. Benzene-d_6 (250 μL) was added. After spectra of the equilibrated solutions were recorded, the tubes were removed from the probe, the desired reactants (4 mmol) were added by syringe, and the solutions were quickly mixed with a vortex stirrer. The tubes were returned to the probe, and spectra were recorded periodically. In each case the first spectrum was recorded with 0.5 min of mixing. Unique ^{13}C NMR signals existed for each compound of interest. This permitted the monitoring of tributylstannyllithium (δ 32.6), hexabutylditin (δ 30.7), tetrabutyltin (δ 8.3, 29.3), and tributyltin hydride (δ 7.7, not observed in these reactions).

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Table 1. Yields of Tributyl(octyl)tin from Reactions of Tributylstannyllithium with n-Octyl Bromide at -20 °C in THF.[a]

Run	[DCP]/[Bu_3SnLi]	% Yield $Bu_3(n\text{-}C_8H_{17})Sn$[b]	% Yield Bu_6Sn_2[c]
1	0	88	12
2	1	71	15
3	4	59	14
4[d]	1	67	26
5[d]	4	54	42

[a]Reactions of 0.5 N Bu_3SnLi (Method B) with n-octyl bromide.

[b]Absolute yields determined by gc comparison to an internal standard.

[c]Absolute yields determined by hplc.

[d]In these reactions the stannyllithium reagent was treated with DCP for 5 minutes at -20 °C before addition to the bromide.

Table 2. Product Yields from the Reactions of Tributylstannyllithium with Cyclohexyl Bromide in THF.[a]

Run	Time (min)	Temp (°C)	Additive (mmol)	% Yield $Bu_3(\underline{c}\text{-}C_6H_{11})Sn$[b]	% Yield Bu_6Sn_2[c]
1	0.5	-20	none	35	18
2	1.0			46	20
3	2.0			58	23
4	5.0			77	26
5	15.0			84	26
6	30	0	none	76	d
7			TBA (1)	64	
8			TBA (2)	70	
9			TBA (4)	68	
10			DCP (1)	12	
11			DCP (2)	10	
12			DCP (4)	6	

[a]Reactions of 0.5 N Bu_3SnLi (Method B) with cyclohexyl bromide.

[b,c]See notes in Table 1.

[d]Not determined.

Table 3. Product Yields from Reactions of Tributylstannyl Anionoids with Cyclopropylcarbinyl Bromide in THF at -20 °C.[a]

Counterion	Method	Additive (equiv)[d]	% Yield Bu_4Sn[b]	1b[b]	2b[b]	Bu_6Sn_2[c]
Li	B	none	6	56	9	29
		none	5	48	9	36
		TBA (1)	6	50	9	32
		TBA (2)	7	55	10	32
		TBA (4)	6	42	8	34
		DCP (1)	4	49	7	34
		DCP (2)	3	49	5	36
		DCP (4)	3	32	5	49
Li[e]	B	none	7	64	10	5
		DCP (2)	3	45	7	13
		DCP (4)	3	41	5	19
Li[e,f]	B	none	5	62	9	4
		DCP (2)	3	48	7	13
		DCP (4)	4	52	8	16
Li	A	none	20	66	11	17
		TBA (2)	20	67	12	15
		TBA (4)	19	66	12	15
		DCP (2)	16	58	5	16
		DCP (4)	17	56	6	15
Li[g]	B	none	20	49	12	28
		TBA (4)	23	48	13	29
		DCP (4)	17	41	8	33

Table 3. (continued)

Counterion	Method	Additive (equiv)	Bu_4Sn	1b	2b	Bu_6Sn_2
K	C	none	26	30	15	22
		TBA (2)	28	32	12	25
		TBA (4)	27	30	13	25
		DCP (2)	20	34	8	32
		DCP (4)	20	29	7	35
K	D	none	7	34	9	h
		TBA (4)	7	35	10	
		DCP (4)	6	35	7	
Cs[i]	E	none	20	25	17	h
		TBA (1)	22	31	18	
		TBA (4)	19	31	15	
		DCP (1)	16	24	14	
		DCP (4)	17	29	14	

[a]See Experimental Section for details.

[b,c]See notes in Table 1.

[d]Equivalents of additive relative to Bu_3SnM.

[e]The cyclopropylcarbinyl bromide used in these alkylations contained a 1 % impurity of 4-bromo-1-butene.

[f]A two-fold excess of cyclopropylcarbinyl bromide was used in these runs.

[g]These reactions contained 1.0 mequiv of lithium tert-butoxide.

[h]Not determined.

[i]Run at -25 °C.

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